PARAMETRIC AND SURFACTANT CHARGE EFFECTS IN THE FLAME ATOMIC SPECTROMETRIC DETERMINATION OF COPPER

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JOSEPH E. IVANECKY III

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IN THE FLAME ATOMIC SPECTROMETRIC DETERMINATION OF COPPER

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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Abstract

The parametric dependence of aerosol ionic redistribution (AIR) for the determination of copper in laminar flame atomic spectroscopy is investigated. Specifically, effects of flame composition, sample uptake rate, and impact bead position are considered. Little dependence is noted, reflecting the high atomization efficiency of the analyte under the varied conditions. Surfactant charge effects, as predicted by the AIR model, were confirmed for both absorption and emission, and characterized with respect to surfactant concentration. In addition to previously reported enhancements with the addition of anionic surfactants, a desensitization was observed with cationic surfactants. The effects of either ionic surfactants were seen to be much larger than surface tension effects as studied using a nonionic surfactant. In emission studies using a total consumption burner no effects of AIR were noted, although an enhancement was observed at high concentrations and is believed to be due to a change in flame conditions.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

A great deal of study has been performed on solvent effects in flame atomic spectroscopy (FAS). Most work has involved the addition of organic compounds, which lower the surface tension of the solution, resulting in a finer aerosol generated during nebulisation and more efficient flame processes. Organic additives can also affect the apparent fuel mixture of the flame (1).

A more limited volume of study has concerned the role of surfactants in such a capacity. The compatibility of surfactants with, and their inherent ability to reduce the surface tension of, aqueous systems would lead one to predict enhanced sensitivity in FAS determinations with surfactant additives. Most reported studies (2,3) have used nonionic surfactants in total consumption emission spectroscopy with no reported success, despite a reduction of surface tension (from 73dynes/cm^2 for water to 30-38dynes/cm^2 for Triton X-100). The inactivity of surfactants in this case has been attributed to the non-equilibrium situation existing at the total consumption nebuliser-burner tip (4). This point was confirmed through surfactant diffusional considerations as presented by Kornahrens (5). An estimate of 10ms was reported for the diffusion of the dodecyl sulfate anion to the droplet surface. Within the constraints of the premix chamber, surfactant redistribution is likely to occur as droplet lifetimes are typically 100-400ms (6). By the nature of its design and operation, the total consumption burner is incapable of allowing sufficient time for this reorientation of the droplet surface.

Because total consumption work represents only a small frac-

tion of all FAS applications, one must still consider the situation of the premixed, laminar flame. In the recent past, several workers have reported observations of enhanced sensitivity with anionic surfactants in premixed flames. Kodama, et al. (7) found chromium absorption to be doubled as sodium dodecyl sulfate (SDS) was added in concentrations up to the critical micelle concentration (CMC), with constant enhancement at higher concentrations. In a later study, Kodama and Miyagawa (8) reported the production of a finer aerosol when surfactants were present and related the observed enhancement to increased atomization efficiency due to smaller droplets. The level of enhancement was also seen to depend upon the analyte, varying inversely with analyte sensitivity.

Venable and Ballad (9) later reported similar results with copper and nickel in the presence of SDS. A slight desensitization was reported in the determination of copper in the presence of a cationic surfactant, tetradecylpyridinium bromide.

Previous work in this laboratory (5) showed a sensitization of copper absorption (using a premixed flame) by the addition of anionic surfactants up to the CMC with a slight decrease in enhancement at higher concentrations. Cationic and nonionic surfactants were found to have little or no effect. A reported dependence upon the oxidant flow rate may be attributed to its effect on droplet distributions. Drawing on the aerosol ionic redistribution (AIR) theory of Borowiec, et al. (10), a charge-dependent theory was proposed for the observed sensitization. The AIR model of Borowiec notes that upon generation of an aerosol, the water-air interface is believed to undergo a reorientation process resulting in the alignment of water molecules with their oxygen

atoms facing outward (11). As a result of polarisation effects, an electrical double layer is established capable of attracting a diffuse layer of cations through a layer of anions. The enhancement mechanism proposed by Kornahrens, et al. is an extension of the AIR theory in which the hydrophobic surfactant molecules accumulate at the droplet surface (due to surface activity) and are capable of attracting ions through charge interactions with their polar head groups. A concentration of the analyte into smaller droplets occurs via a stripping action during the break up of large droplets in the nebulisation process. The drop off in enhancement observed above the CMC was attributed to the analyte binding to the micelles within the bulk solution, reducing the surface concentration ans subsequent stripping effect.

This study serves as an extension of the earlier work with a particular emphasis on improving and characterising the parameters affecting the reproducibility of the enhancement of copper determinations. Factors to be studied include flame compositon, sample uptake rate, impact bead position, and observation height.

Testing for AIR effects in premixed flame emission spectroscopy was also undertaken. Because AIR is a nebulisation phenomenon, it should be expected in any premixed flame method. Extension to emission should be straightforward, but has not yet been reported. A successful outcome should corroborate the AIR model.

The final objective of this study was to assess the effect of surfactant charge, with respect to the AIR model, in total consumption emission spectroscopy. Because AIR in premixed flames relies on preferential sampling of analyte-enriched small droplets, and since there is no similar drop-size bias with total consumption

burners, the AIR mechanism was not expected to be operable in total consumption experiments. However, other surfactant effects were possible, including improvement in atomization efficiency by a reduction in droplet size or a change in flame chemistry (due to the fuel-like hydrocarbon nature of the surfactant additives). These effects should have charge and concentration dependences different from those observed in studies with premixed flames.

II. EXPERIMENTAL

Reagents. All copper solutions were prepared from a 1000ppm stock solution. Reagent grade $Cu(NO_3)$ $3H_2O$ (Allied Chemical Co.), SDS (MCB), Triton X-100 (TX-100; Sigma), and cetyltrimetylammonium bromide (CTAB; Sigma) were used without prior purification. All glassware was triply rinsed with distilled, deionized water prior to use. Solutions were made with distilled, deionized water treated in a Millipore filtration system. Solutions were generally used between one and 24h of preparation after mixing. In a separate study, sclutions were shown to exhibit no time-dependent characteristics over a period of several weeks.

Procedure and Apparatus. A Perkin-Elmer 4000 atomic absorption spectrophotometer was used with a long path, premix burner and an air-acetylene flame for all absorption studies (except where noted). All such studies were corrected for background absorption using a deuterium lamp. While this instrument was equipped with a variable rate nebulizer for use in the uptake rate study, investigation of impact bead position was limited to a single position by the design of the manufacturer.

A GCA/McPherson Model EU-703-70 AA/AE/AF spectrophotometer was utilized in all emission studies. The McPherson set-up was equipped with one of two Varian Techtron long path burners for premixed, laminar flames (a 5cm slot with nitrous oxide-acetylene for AE work, and a 10cm slot with air-acetylene for AA to provide instrumental comparison with the Perkin-Elmer). This set-up also employed a varialbe rate nebulizer and an adjustable impact bead which made parametric studies feasible. Total consumption emission studies used the same McPherson spectrophotometer equipped with a Beckman

hydrogen-oxygen atomizer-burner. Surface tension measurements were performed on a du Nuoy tensiometer with a platinum ring calibrated against standard solutions of water and acetonitrile (73.05 and 29.30dynes/cm^2, respectively).

Sensitivity was defined to be the slope of a best fit, least squares linear calibration curve consisting of signal values for six Cu^{2+} concentrations evenly spaced between 0 and 10ppm. Parametric optimization was performed with solutions containing zero and 2mM SDS. Systematic error and instrumental drift was minimized by randomly sampling solutions of varying copper concentrations and a given SDS concentration. In the case of surfactant concentration studies, sets of solutions at a given surfactant concentration were run in random order.

Enhancement was calculated as follows:

$$\% \text{ Relative Enhancement} = \frac{(\text{slope})_{surf} - (\text{slope})_o}{(\text{slope})_o} \times 100\%$$

where $(\text{slope})_{surf}$= the slope of a calibration curve for solutions containing a given concentration of a given surfactant, and $(\text{slope})_o$ = the slope of a calibration curve for solutions containing no surfactant. All determinations (absorption and emission) were performed at the 324.8nm line.

In the flame condition studies, and all remaining determinations, gas flow rates were measured using Matheson flowmeters (rotameters). Flows measured were corrected for density and pressure.

III. RESULTS AND DISCUSSION

Premix Burners.

Flame Conditions. Due to the influence of oxidant flow rates on the aerosol droplet size distributions (5), a single oxidant flow rate was maintained throughout the study and the fuel flow rate was increased to provide higher fuel percentages. Figure 1 illustrates the dependence of an AA determination of Cu on the flame composition, using 0 and 2mM SDS. Two important features are evident. First, there is clearly an enhancement of sensitivity with the addition of SDS. This is consistent with the findings of Kornahrens and Kodama, confirming a real change in sensitivity (represented by the slope of the calibration curve), and not simply a change in intercept. Secondly, the sensitivity (with or without surfactant) does not vary significantly with percent fuel until conditions are sufficiently fuel rich to create a luminous flame, where sensitivity and enhancement decrease sharply. The possibility of aerosol dilution by the higher total gas flows at such conditions is not a likely possibility as sensitivity dropped nearly 14% when percent fuel was increased from 16.7% to 21.5%, representing an increase in gas flow of only 6%. A dilution effect would be expected to produce a more gradual change with increasing flow. A second possible explanation could be an increase (with increasing fuel) of vaporization interferences. However, this should be accompanied by changes in vertical flame profiles. Because there is no detectable change in the atom distribution within the flame, this alternative is also unlikely. The most probable explanation may therefore be spectral interference from flame luminosity. The wide range of flame con-

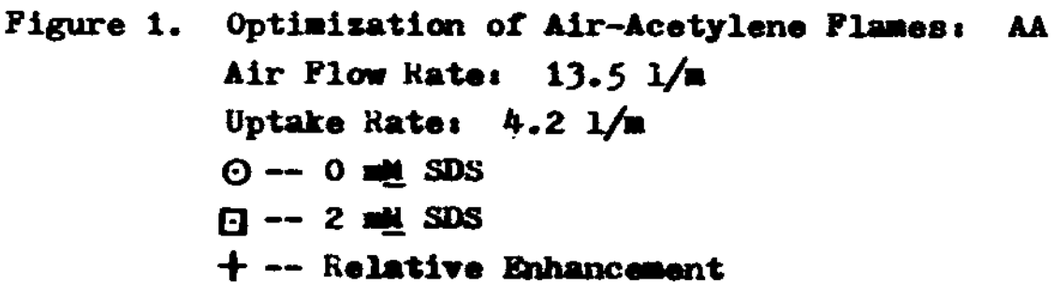
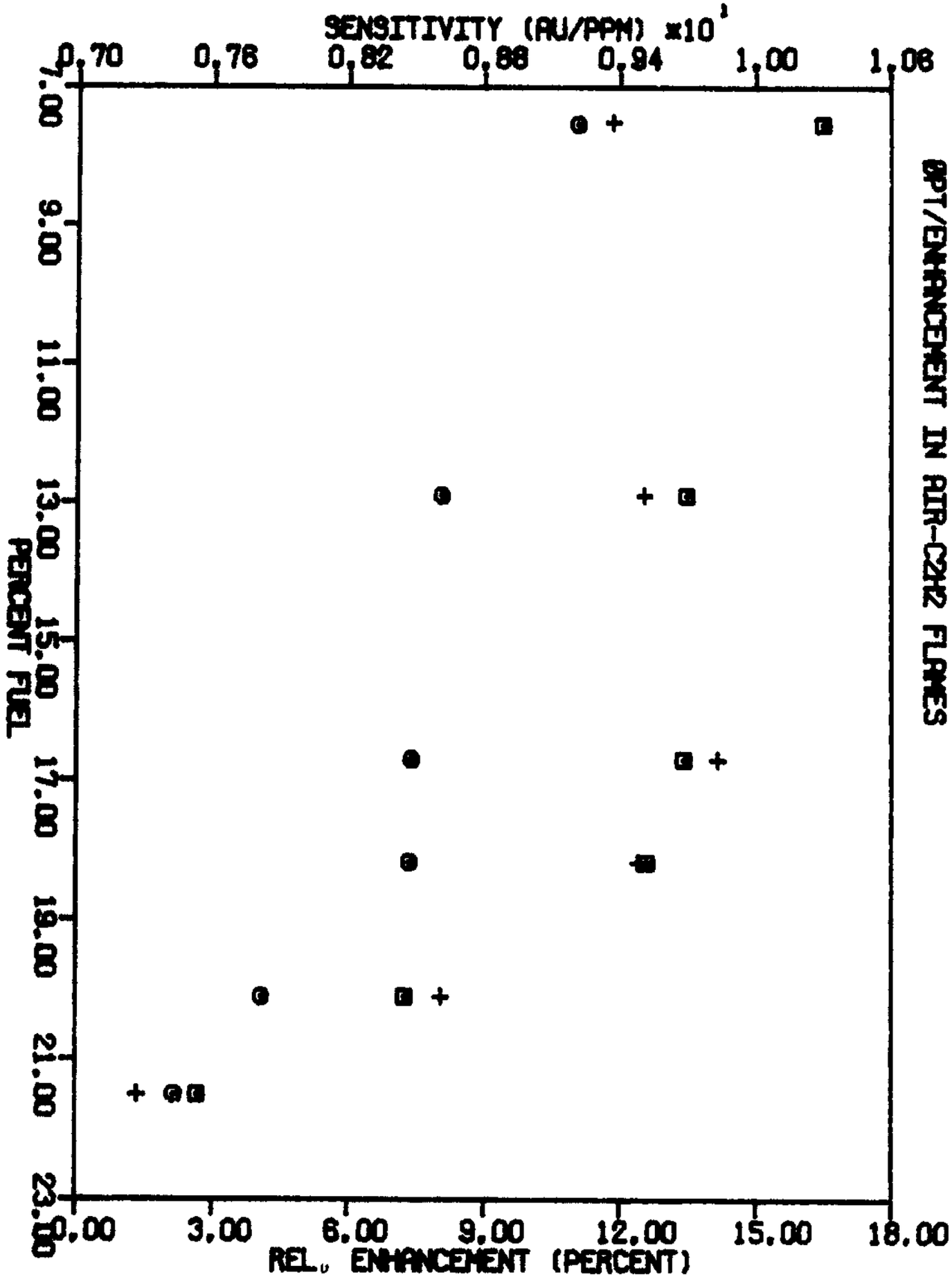


Figure 1. Optimization of Air-Acetylene Flames: AA
Air Flow Rate: 13.5 l/m
Uptake Rate: 4.2 l/m
⊙ -- 0 mM SDS
⊡ -- 2 mM SDS
+ -- Relative Enhancement


SENSITIVITY (AU/PPM) x10
0.70
0.76
0.82
0.88
0.94
1.00
1.06
7.00
9.00
11.00
13.00
15.00
17.00
19.00
21.00
23.00
PERCENT FUEL
OPT/ENHANCEMENT IN AIR-C2H2 FLAMES
0.00
3.00
6.00
9.00
12.00
15.00
18.00
REL. ENHANCEMENT (PERCENT)

ditions over which the sensitivity remains relatively constant and high has been partly attributed to the low dissociation energy of copper oxide (12,13). In general, air-acetylene flame composition appears to have little effect upon the magnitude of enhancement except in luminous flames, where overall sensitivity is low. This is consistent with the AIA model, because AIA is a nebulisation phenomenon and would not be expected to exhibit a dependence upon flame composition. Because reproducibility should be improved in leaner flames (sensitivity appears to be nearly independent of percent fuel from 10% to 18%) the leanest stable flame composition was used (approximately 12% fuel).

Results of a similar experiment performed with a nitrous oxide -acetylene flame used in emission studies are given in figure 2. The level of enhancement is roughly constant throughout the study, with relatively large random deviations. The observation of an overall optimal flame composition in the nitrous oxide flame may result from temperature variations or possible formation of carbonaceous compounds forming in fuel-rich flames. Emission studies exhibit a greater sensitivity to temperature as atoms must be excited following atomisation. The existence of an optimal flame condition would appear to indicate a maximization of flame temperature resulting in the greatest energy transfer to the analyte. Based on this information, future AE studies employed nitrous oxide -acetylene flames with 29-31% fuel (versus 17% as stoichiometric).

Aspiration Rate Effects. When investigating the effects of solution uptake rate on sensitivity, optimal flame conditions were chosen consistent with the findings reported above. Beginning with the lowest aspiration rate, sensitivities were measured with

Figure 2. Optimisation of Nitrous Oxide-Acetylene Flames: AE
N_2O Flow Rate: 9.9 l/m
Uptake Rate: 3.4 ml/m
⊙ -- 0 mM SDS
⊡ -- 2 mM SDS
+ -- Relative Enhancement

OPT/ENHANCEMENT IN N2O-C2H2 FLAMES AE
SENSITIVITY (AMPS/PPM) x10⁹
REL. ENHANCEMENT (PERCENT)
PERCENT FUEL
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
10.00
13.50
17.00
20.50
24.00
27.50
31.00
34.50
38.00

0 and 2mM SDS and the uptake rate was then stepped through the range of study, roughly 1 to 8ml/m. Figures 3 and 4 illustrate the results of this experiment for AA and AE determinations, respectively. Several trends are evident. First, there is a non-linear relationship between sensitivity and uptake rate. This occurs in both studies regardless of surfactant concentration, indicating an overall transport phenomenon. Secondly, allowing for random experimental deviations, the relative enhancement does not appear to exhibit any dependence upon uptake rate. There is one noteworthy difference between AA and AE results. In contrast to the AE study, the AA investigation exhibits no optimal uptake rate in terms of sensitivity. This may be attributed to the improvement of transport efficiency by an auxiliary air flow found in the Perkin-Elmer (AA), but not in the GCA/McPherson (AE)(14). Auxiliary air is a fraction of the total oxidant flow which enters the gas stream through the side of the spray chamber, rather than through the nebuliser. The effects of auxiliary flows are mixed. While decreasing gravitational settling losses, auxiliary air increases losses through coalescence. When choosing an aspiration rate for further studies, Howarth, et al. (15) found rates of 2-3ml/m provided the best compromise between sensitivity, flame stability, and sample usage. In keeping with these findings and the results obtained here, a slightly higher range of rates, 3-5ml/m, was used. This was preferred because the variation of sensitivity with uptake rate over this selected range was smaller than that over the range suggested by Howarth.

Because many variables are involved in the nebulisation and transport of the sample to the flame, the explanation of their ef-

Figure 3. Optimization of Uptake Rate in Air-C_2H_2 Flames: AA
Air Flow Rate: 13.5 l/m
C_2H_2 Flow Rate: 1.5 l/m (15.0%)
⊙ -- 0 mg SDS
⊡ -- 2 mg SDS
+ -- Relative Enhancement

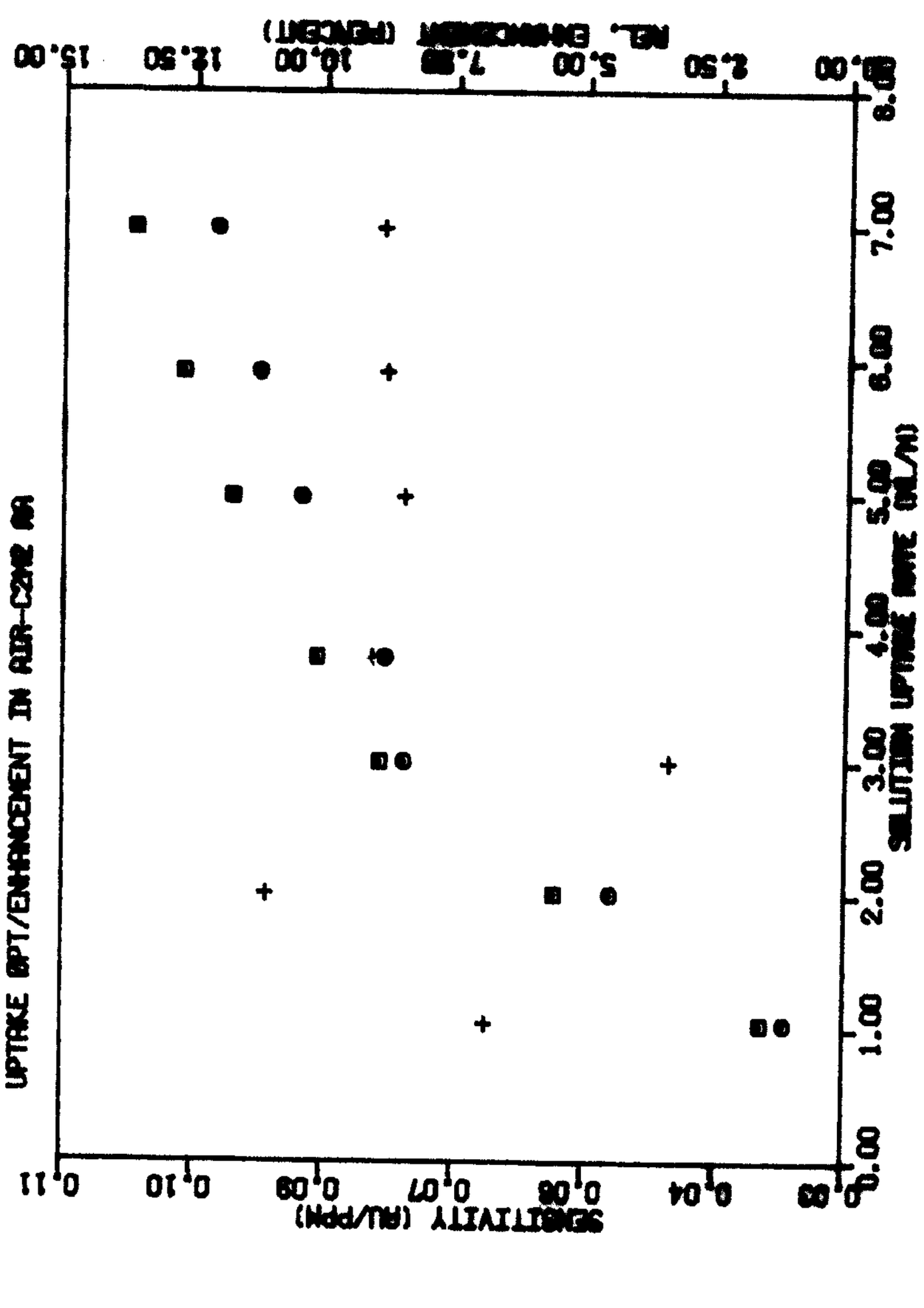
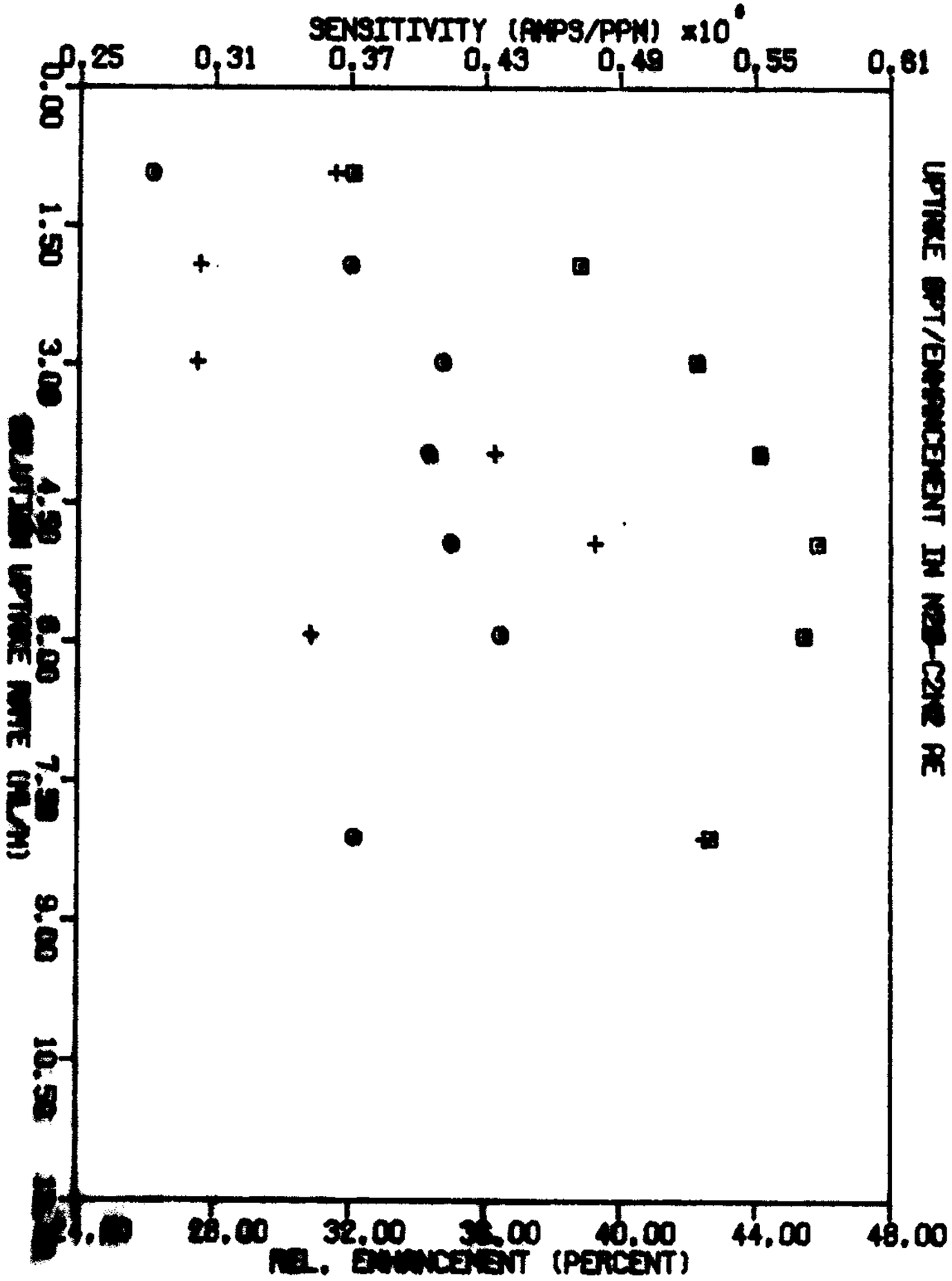

UPTAKE @PT/ENHANCEMENT IN AIR-C2H2 @A
SOLUTION UPTAKE RATE (NL/M)
SENSITIVITY (AU/PPM)
MAL. ENHANCEMENT (PERCENT)
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
0.00
0.04
0.08
0.07
0.09
0.10
0.11
2.50
5.00
7.50
10.00
12.50
15.00

Figure 4. Optimization of Uptake Rate in N_2O-C_2H_2 Flames: AE
N_2O Flow Rate: 9.9 l/m
C_2H_2 Flow Rate: 3.7 l/m (27.2%)
⊙ -- 0 mM SDS
⊡ -- 2 mM SDS
┼ -- Relative Enhancement


SENSITIVITY (AMPS/PPM) x10
0.25
0.31
0.37
0.43
0.49
0.55
0.61
0.00
1.50
3.00
4.50
6.00
7.50
9.00
10.50
28.00
32.00
40.00
44.00
48.00
REL. ENHANCEMENT (PERCENT)

fects becomes complicated and often overlapping. For example, the solvent is able to exert an effect upon the flame. Howarth, et al. (15) proposed an increased oxidizing environment within the flame as oxygen concentration increases with the introduction of an oxygen-containing solvent. This would lead to improved sensitivity with the air-acetylene flame, as the fuel percentage would be decreased (see fig.1). However, such effects should be minimal in this case, because the amount of solvent-derived oxygen reaching the flame is small with respect to the gas flow rates, and because the determination is relatively insensitive to changes in composition in the region of study. A different solvent effect which might be more important here is the saturation of the gas stream by the solvent. Dependent on the vapor pressure of the solvent and temperature of the gas mixture, saturation generally occurs at uptake rates exceeding 3ml/m (16). This results in diminished vaporization and therefore, formation of larger droplets. This in turn increases collisional and gravitational losses (see below), decreasing the overall mass transport efficiency.

Table One shows how the sample volume reaching the flame varies with the observed uptake rate. The volume of sample in the flame was determined by the difference between measured uptake and the volume of waste collected over an extended period of sample introduction. The reported volume efficiency is the percent (vol) of sample which reaches the

Table One. Transport Efficiencies in Premixed Burners.
Air Flow Rate: 11.3 l/m
C_2H_2 Flow Rate: 1.7 l/m

Observed Uptake Rate, ml/m (mM SDS)	Sample Reaching Flame, ml/m	Transport Efficiency(%)
2.66 (0)	0.46	17.3
2.74 (4)	0.46	16.8
2.86 (2)	0.47	16.4
4.76 (4)	0.60	12.6
5.32 (2)	0.58	10.9
5.66 (0)	0.54	9.5
7.19 (2)	0.47	6.5
7.46 (0)	0.51	6.8

Figure 5. Volume Transport Efficiency versus Uptake Rate
Air Flow Rate: 11.3 l/m
C_2H_2 Flow Rate: 1.7 l/m (13.0%)
⊙ -- 0 mM SDS
⊡ -- 2 mM SDS
+ -- 4 mM SDS

TRANSPORT EFFICIENCIES IN PREMIX BURNERS
TRANSPORT EFFICIENCY (PERCENT)
0.00
3.00
6.00
9.00
12.00
15.00
18.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
OBSERVED UPTAKE RATE (ML/M)

flame. The same data is summarised in figure 5. In this limited study (which includes results with 0, 2, and 4mM SDS), it is clear that the surfactant dos not affect the uptake efficiency, since a single curve appears to encompass all data (fig.5).

With a variable rate nebulizer, the oxidant flow rate is inversely related to the uptake rate (15). The initial increase in signal with uptake rate may then be the result of a concentration of the sample within the gas stream. An eventual increase in large droplet populations with decreased nebulising gas flow could reduce evaporation efficiency and explain the plateau and slight decrease in signal at high uptake rates. Collisional losses may also be involved in the decreased sensitivity at high aspiration rates, as the collisional frequency is proportional to the square of the droplet density (number of droplets per unit volume). An extension of collisional processes encompasses the possible loss of signal in AE due to collisions occurring within the flame. As more droplets reach the flame, there may be a "quenching" of excited atoms through a collision with a droplet or desolvated particle, reducing the signal. For elements sensitive to vaporisation interferences (i.e. Ca) there may thus be an optimum flow rate representing a compromise between sensitivity and interference effects.

Depending upon the gas flows encountered, there are two other types of losses which should be considered: gravitational settling and impaction. At high uptake rates, lower flows can result in longer transport times. This, combined with larger droplet sizes due to coalescence resulting from collisions at high aerosol densities, increases losses due to gravitational settling (17).

On the other hand, high gas flows impart greater momentum to the aerosol and losses increase through collisions with the spray chamber. Both processes tend to shift droplet distributions to smaller diameters, although they are brought about by opposing conditions. In a study with a dual concentric spray chambered ICP system. Browner (17) showed that despite a decrease in nebulization efficiency with uptake rate, the useful mass transport rate, defined as the flow of analyte contained in droplets contributing at least 10% to the signal, remains relatively constant. This important since ICP and premix FAS systems are very similar with respect to sample transport.

Impact Bead Position. A further consideration must be made when using an impaction surface, such as a mixer paddle or impact bead, as was employed in these studies. While removing large droplets, the bead also serves to provide secondary fragmentation of the aerosol.(The efficiency of such surfaces is improved in the absence of auxiliary air flows (14). This may be attributed to increased turbulence as auxiliary air tends to flow around the walls of the spray chamber before mixing with the aerosol.) In figure 6 one sees the effect on sensitivity of positioning the impaction bead. While there appears to be an optimal position with respect to sensitivity, the observed enhancement appears to exhibit no such dependency. A similar optimization was reported by Kouth (18) and expained by improved droplet size and number reaching the flame. In further studies a position of 1.25mm was used.

Surfactant Charge Effects. Figures 7-10 clearly illustrate the dependence of the sensitization mechanism on surfactant charge. As would be expected, figs. 7 and 8 show a similar trend in enhan-

Figure 6. Optimization of Impact Bead Position in AE
N_2O Flow Rate: 9.9 l/m
C_2H_2 Flow Rate: 3.7 l/m (27.2%)
Uptake Rate: 4.0 ml/m
⊙ — 0 mM SDS
⊡ — 2 mM SDS
+ — Relative Enhancement

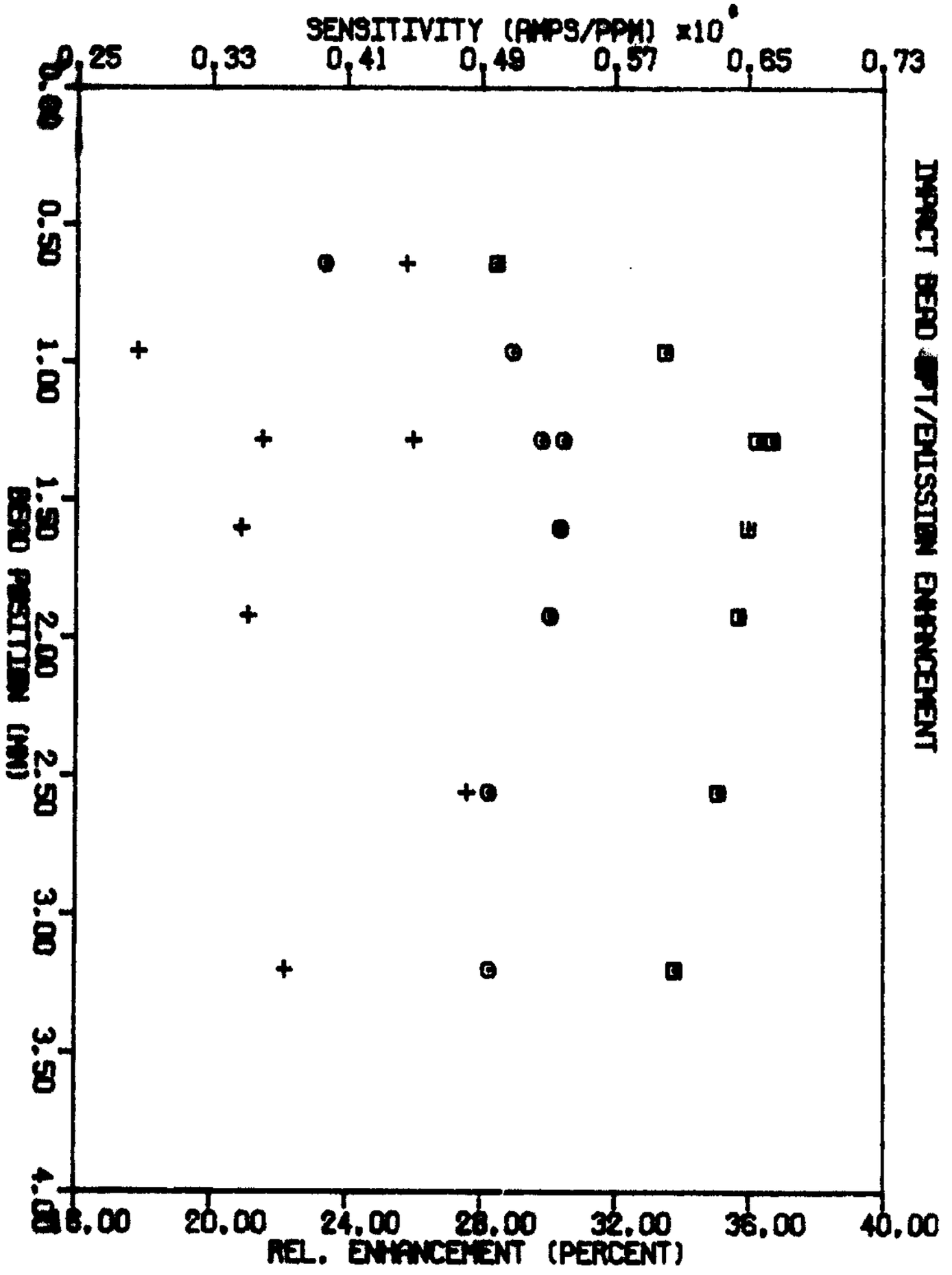
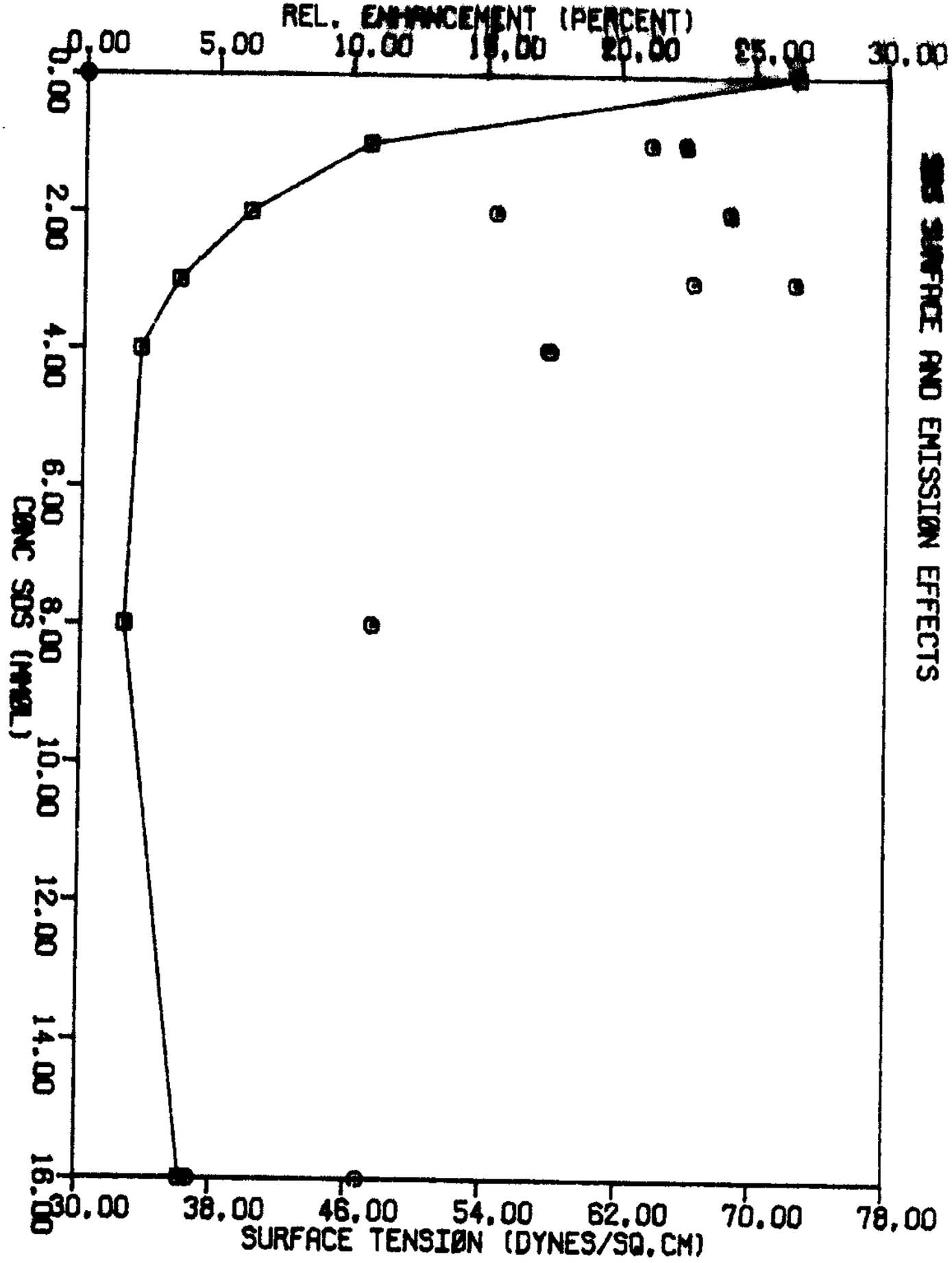

SENSITIVITY (AMPS/PPM) x10
0.25
0.33
0.41
0.49
0.57
0.65
0.73
0.0
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
16.00
20.00
24.00
28.00
32.00
36.00
40.00
REL. ENHANCEMENT (PERCENT)
INFRARED BEAM POSITION (MM)
IMPACT BEAM/EMISSION ENHANCEMENT

Figure 7. Surface Tension and Absorption Effects of SDS in AA
Air Flow Rate: 14.5 l/m
C_2H_2 Flow Rate: 1.5 l/m (9.4%)
Uptake Rate: 2.9 ml/m
⊙ -- Perkin-Elmer
⊡ -- GCA/McPherson
+ -- Surface Tension

SDS SURFACE AND ABSØRPTIØN EFFECTS
REL. ENHANCEMENT (PERCENT)
0.00
3.00
6.00
9.00
12.00
15.00
18.00
SURFACE TEN. (DYNES/SQ.CM)
30.00
38.00
46.00
.00
62.00
70.00
78.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
CONC SDS (MMOL)

Figure 8. Surface Tension and Emission Effects of SDS
N_2O Flow Rate: 9.9 l/m
C_2H_2 Flow Rate: 3.7 l/m (27.2%)
Uptake Rate: 5.1 ml/m
⊙ --Relative Enhancement
⊡ --Surface Tension


REL. ENHANCEMENT (PERCENT)
0.00
5.00
10.00
15.00
20.00
25.00
30.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
CONC SDS (MMOL)
30.00
38.00
46.00
54.00
62.00
70.00
78.00
SURFACE TENSION (DYNES/SQ.CM)
SURFACE AND EMISSION EFFECTS

cement with SDS concentration for the absorption and emission analyses. Sensitisation is observed to increase to a maximum with increasing SDS monomer concentration, followed by a decrease in the effect with the formation of micelles upon reaching and exceeding the CMC. The magnitude of this post-CMC effect depends on the degree of association of the analyte with the micelle, which has been shown previously to be more complex than merely a charge effect (19).

The hotter, higher velocity, nitrous oxide-acetylene flame utilized in emission studies yielded a maximum enhancement nearly 65% greater than the air-acetylene flame employed in atomic absorption studies. The droplet size distribution has been shown to influence the lateral distribution within the flame. A lateral narrowing of the aerosol distribution has been observed with increasing solute concentrations, resulting from larger particles and less lateral diffusion (20). Such an effect is not generally observed in the air-acetylene flame, as gas velocities are typically 2-3 times lower than those incurred with the nitrous oxide burner (due to a faster burning velocity). Unfortunately no evidence of this phenomenon could be detected in the lateral profiles measured with various surfactant concentrations. As of this time, a sufficient explanation has not been found for the greater sensitisations observed with the nitrous oxide-acetylene flame over the air-acetylene flame. A combination of fuel mix and AIR effects is possible.

As expected, although only briefly reported by Venable and Ballad (9), the addition of a cationic surfactant, CTAB, desensitized the analysis. With a positively charged surface (brought about by the CTA^+ cation), the analyte is repulsed from the sur-

face. Consequently there is depletion of the analyte from the small droplets generated from the surface material upon nebulisation, as described by the AIA model. Upon formation of cationic micelles at and above the CMC, the precision of the analysis is seen to decrease substantially (see fig.9). This may be attributed to opposing charge repulsion effects, as the analyte is not only repulsed from the surface, but also from the bulk region by the micelles. Another possibility is the increase in solution viscosity with surfactant concentration and possible effects on uptake rate.

Surface Tension Effects. Surface tension was studied independently from AIA effects by the addition of TX-100. Figure 10 illustrates the effect of decreased surface tension in premix AE. Although random scatter appears within the data, the overall magnitude of the effect is seen to be small. Some of this apparent insensitivity to surface tension effects may be due to the fact that copper is atomised very efficiently in air-acetylene (21) and nitrous oxide-acetylene flames (13).

A decrease in surface tension has been shown to be accompanied by a lower mean droplet diameter (8). This effect can be induced by the addition of surfactant, in which case it is maximised at concentrations at, or above, their CMC. Decreases in droplet diameter also allow for more efficient production of dry salt particles as evaporation efficiency increases due to the inverse proportionality between surface area per unit mass and particle diameter (22). As a result, reaction with the flame occurs faster as the aerosol has a greater surface area. This effect is likely to be limited, in most cases, by saturation of the gas stream. For easily atomised elements saturation is not critical as large drop-

Figure 9. Surface Tension and Emission Effects of CTAB in AE
H_2O Flow Rate: 7.6 l/m
C_2H_2 Flow Rate: 3.7 l/m (30.9%)
Uptake Rate: 5.1 ml/m
⊙ --Relative Enhancement
⊡ --Surface Tension
Error bars represent the standard deviation of the measurement, as evaluated after three trials.

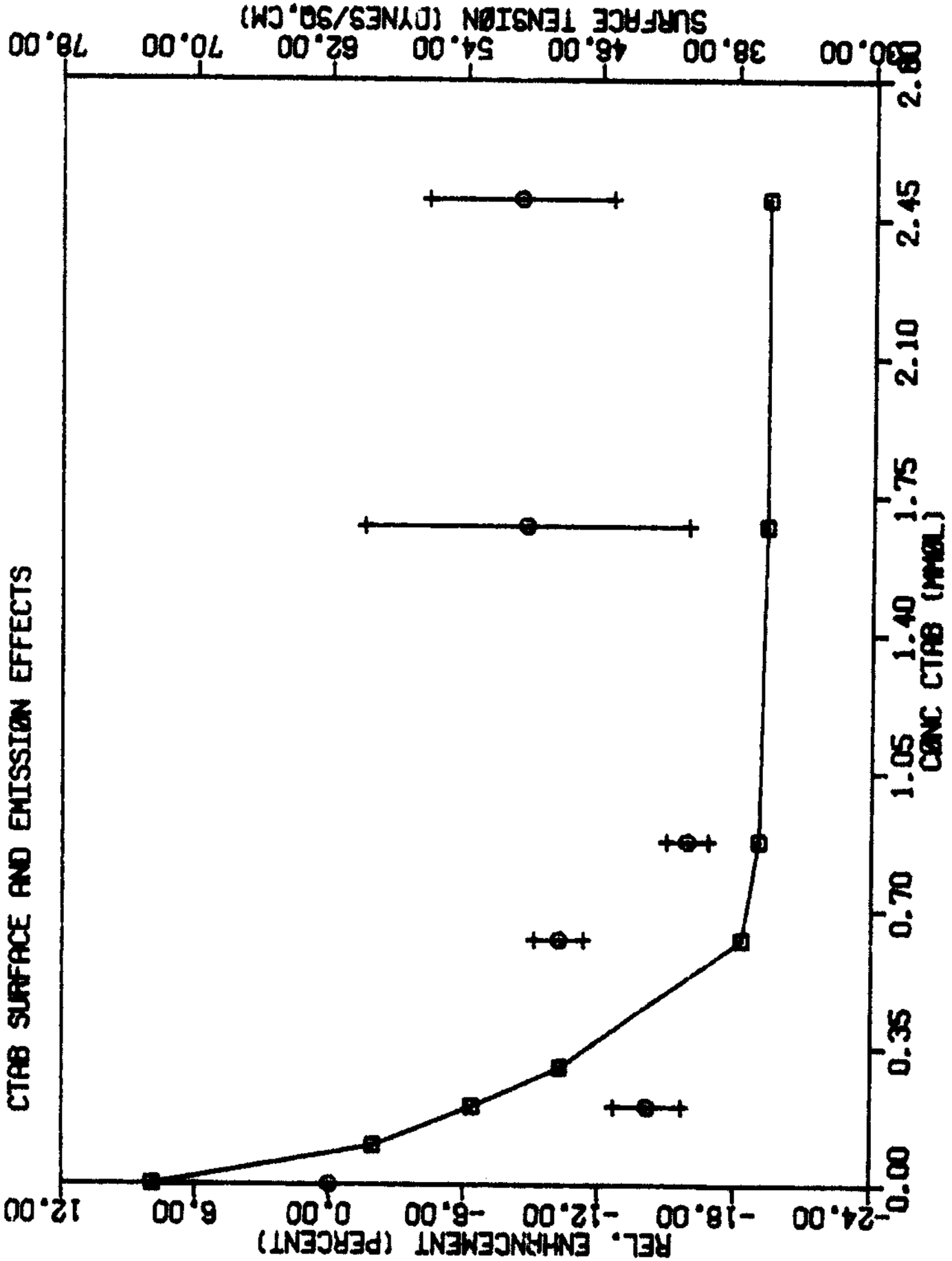

CTAB SURFACE AND EMISSION EFFECTS
SURFACE TENSION (DYNES/90.CM)
30.00
38.00
46.00
54.00
62.00
70.00
78.00
REL. ENHANCEMENT (PERCENT)
12.00
6.00
0.00
-6.00
-12.00
-18.00
-24.00
CONC CTAB (MMOL)
0.00
0.35
0.70
1.05
1.40
1.75
2.10
2.45
2.80

Figure 10. Surface Tension and Emission Effects of TX-100 in AE

N_2O Flow Rate: 7.6 l/m

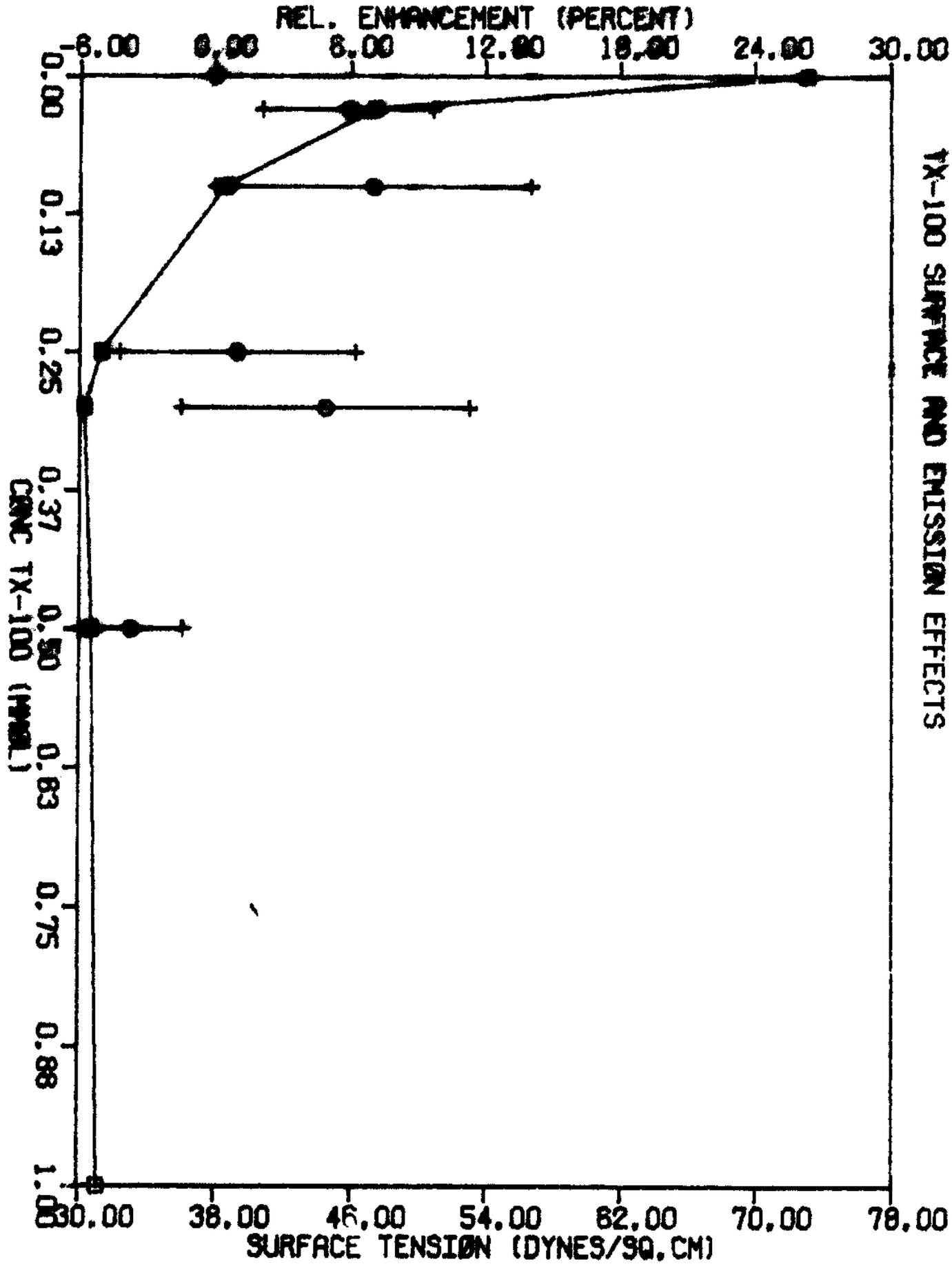
C_2H_2 Flow Rate: 3.4 l/m (30.9%)

Uptake Rate: 5.0 ml/m

⊙ --Relative Enhancement

⊡ --Surface Tension

Error bars represent the standard deviation of the measurement, as evaluated after three trials.


REL. ENHANCEMENT (PERCENT)
-6.00
0.00
6.00
12.00
18.00
24.00
30.00
0.00
0.13
0.25
0.37
0.50
0.63
0.75
0.88
1.00
CONC TX-100 (MMOL)
TX-100 SURFACE AND EMISSION EFFECTS
30.00
38.00
46.00
54.00
62.00
70.00
78.00
SURFACE TENSION (DYNES/SQ.CM)

lets may contribute to the signal. Mouth (18) has shown the aerosol median droplet diameter increases upon passage through the burner slot. A point of further study is the opposing effects of coalescence within the burner slot and droplet diameter reduction by the addition of surfactants. Despite the positive effects of reducing surface tension as discussed, their role in a sensitization of the determination appears to be much smaller than charge considerations.

Total Consumption Burners

Flame Conditions. Based on premix results, it was assumed the addition of SDS would not affect optimum conditions, so optimization experiments were performed with no SDS. When determining optimal flame conditions in the hydrogen-oxygen total consumption burner, the oxidant flow rate remained fixed to provide a constant solution uptake rate. The best sensitivity was obtained with fuel-rich conditions, see figure 11. This was attributed to the burning of excess fuel with entrained air. Throughout the remaining studies with this set-up a burning mixture with about 75% fuel was used (slightly richer than the 67% stoichiometry).

The total consumption burner was not equipped with a variable rate nebuliser so uptake rate could not be studied independent of flame composition. The gas flows used, 3.1l/m of C_2 and 9.3l/m H_2, were chosen on the basis of optimal flame composition and signal stability (dependent upon sufficient sample delivery). Results of Foster and Hume (3) indicate that independent variation of uptake rate affects flame temperature sensitively. This is particularly important with elements characterized at high energy lines, as sensitivity for these determinations was optimized at lower rates.

Figure 11. Optimization of Hydrogen-Oxygen Flames: AE
Total Consumption
O_2 Flow Rate: 5.8 l/m
Uptake Rate: 1.95 ml/m

OPT. IN H2-02 FLAMES TC AE
SENSITIVITY (AMPS/PPM) x10⁶
0.00
0.04
0.08
0.12
0.16
0.20
0.24
50.00
54.00
58.00
62.00
66.00
70.00
74.00
78.00
82.00
PERCENT FUEL

Since copper has a much higher excitation energy than the alkali metals studied by Foster and Hume, the optimum uptake rate would probably be impracticably low. Regardless of these considerations, a sound assessment of AIR under the stated experimental conditions can be made.

At the low uptake rates encountered here, 0.5-0.8 ml/m, the expected signal should be proportional to the solution flow (23). Assuming laminar sample flow through the uptake capillary (as described by the Hagen-Poisseuille law)(23), the nebulisation rate should be inversely proportional to the solution viscosity. Additionally, the Nukiyama-Tanasawa equation (24) for estimating the mean droplet diameter of such aerosols, predicts increasing size with solution viscosity to a small extent.

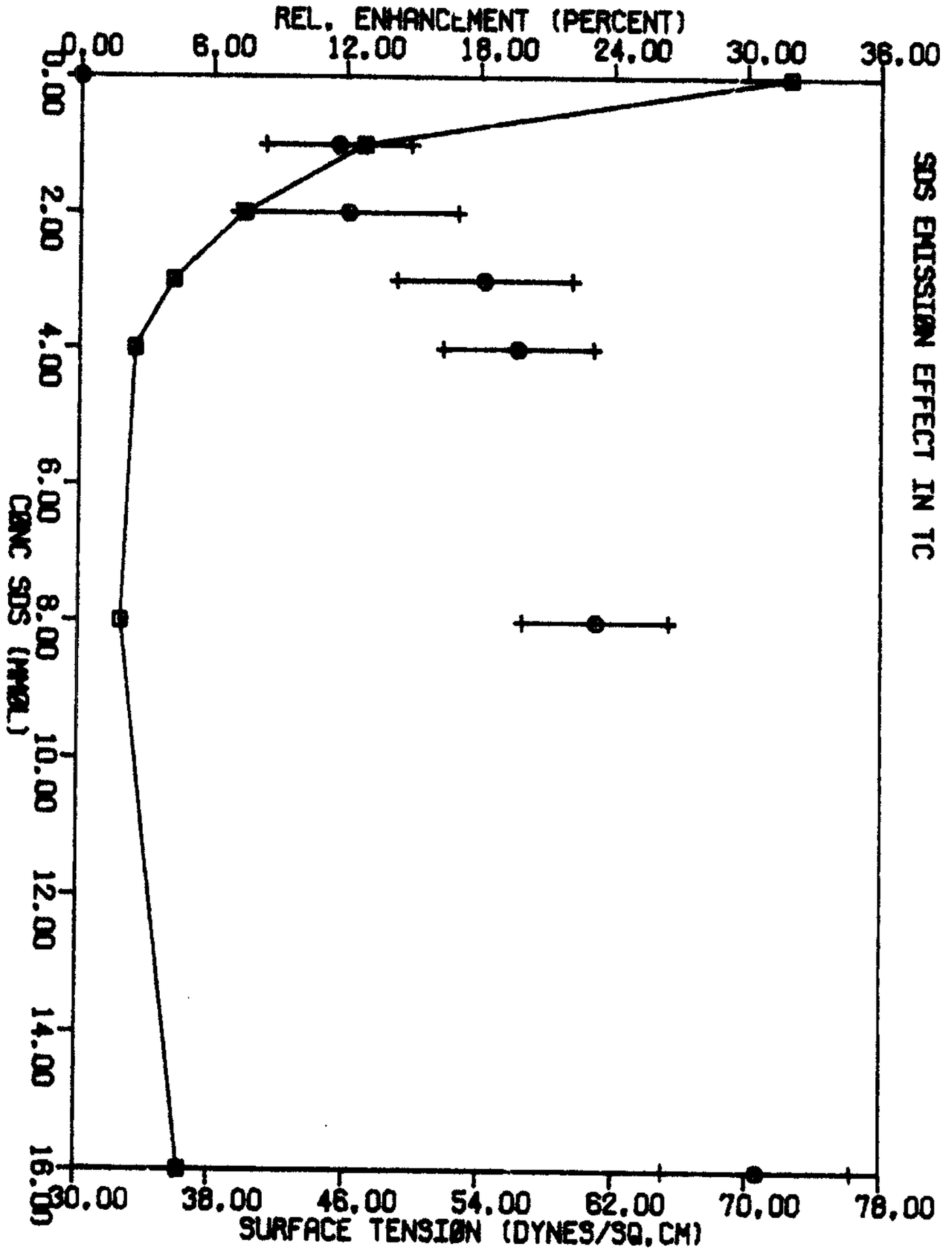
Pungor and Mahr (23) also predict improved dispersity of the aerosol and subsequently more efficient emission with decreases in surface tension. The Nukiyama-Tanasawa equation offers no firm predictions on the effects of surface tension. As discussed in the introduction, surfactants must diffuse to the surface to exert an influence on surface tension, and the time scale of nebulization in the total consumption burner may not allow for such diffusion. In fact, the data presented in figure 12 shows no clear relationship between surfactant concentration and sensitivity or resulting equilibrium surface tension, indicating that, indeed, equilibrium conditions do not apply.

This suggests that the sensitivity enhancement induced by SDS (figure 13) is not attributable to the decrease in surface tension as no similar trends were obtained with solutions of TX-100 or CTAB (fig. 12) with comprable surface tension. Instead, the effect is

Figure 12. Emission Effects of TX-100 and CTAB in AE
Total Consumption
O_2 Flow Rate: 3.1 l/m
H_2 Flow Rate: 9.3 l/m (75.0%)
Uptake Rate: 0.81 ml/m
⊙ -- TX-100 (Two trials)
⊡ -- CTAB

TX-100 CTAB EMISSION EFFECTS IN TC
REL. ENHANCEMENT (PERCENT)
12.00
8.00
0.00
-8.00
-12.00
-18.00
-24.00
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
CONC SURFACTANT (MMOL)

Figure 13. Surface Tension and Emission Effects of SDS in AE Total Consumption
O_2 Flow Rate: 3.1 l/m
H_2 Flow Rate: 9.3 l/m (75.0%)
Uptake Rate: 0.78 ml/m
⊙ --Relative Enhancement
⊡ --Surface Tension
Error bars represent the standard deviation of the measurement, as evaluated after three trials.


REL. ENHANCEMENT (PERCENT)
0.00
6.00
12.00
18.00
24.00
30.00
36.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
CONC SDS (MMOL)
SDS EMISSION EFFECT IN TC
30.00
38.00
46.00
54.00
62.00
70.00
78.00
SURFACE TENSION (DYNES/SQ.CM)

ascribed to possible increases in flame fuel, noting the similarity between curve shape in figs. 11 and 13. SDS is present in approximately a 14-fold excess (w/w) with respect to TX-100 and 42 times more concentrated than CTAB. In a limited study, TX-100 produced levels of enhancement comprable to those observed with SDS, when present in similar amounts (by weight, relative enhancement of about 23% for 7.4mM TX-100). AIR does not appear to exist in the total consumption burner, as evidenced by the difference in enhancement dependence upon SDS concentration. No decrease is noted at concentrations above the CMC in fig. 13.

IV. CONCLUSIONS AND FUTURE RESEARCH

From the parametric study conducted with and without surfactant, little dependence of the enhancement mechanism was noted, with the exception of conditions where the overall determination decreased (i.e. luminous air-acetylene flames). Some of this insensitivity to experimental parameters has been attributed to the element studied here and its apparent freedom from most interferences encountered in FAS. Additionally, the dependence of the magnitude of the effect, upon the flame used must be explained.

Confirmation of surface tension effects and the non-applicability of AIR to the total consumption burner were observed. A fuel effect was proposed for an observed increase in signal when high concentrations of the organic surfactants were present, while no charge dependence was noted. Future work in this area should include a study of different types of surfactants present in concentrations adding equimolar amounts of potential organic fuel.

Finally, the dependence upon surfactant charge was also confirmed with cationic surfactants, with a proposed repulsion-based theory on the concentration dependent desensitisation observed.

Further experimentation is needed not only in researching the magnitude of the effect with different analytes, but also within the more complex matrices commonly encountered in the typical FAS determination. The fundamental study of aerosol generation and transport with respect to the addition of surfactants remains a field for study.

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